Fractal approach to the β relaxation in supercooled liquids

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In the present work we present a fractal model for the β relaxation in supercooled liquids. The macroscopic dynamics is obtained by superposition of relaxation of independent mesoscopic regions (cages). Scaling relations and exponents are assumed for the distribution of cage sizes and for the size dependent response of the independent cages. In this way we obtain some scaling relations for the average response, in the time and frequency domain. For a particular choice of the scaling exponents we obtain the scaling relations predicted by the MCT. The comparison with recent light scattering data reveals that the scaling exponents of the distribution of cage sizes are universal but the single cage relaxation depends on the detailed material structure.

61.20.Lc, 64.70.Pf, 61.43.H

I. INTRODUCTION

The liquid-glass transition at the calorimetric temperature T_g has been a subject of extensive experimental and theoretical study for many years. However, more recently the interest has been shifted to the range of supercooled liquid temperatures, which is extended from T_g to the melting temperature T_m. Light-scattering experiments in this range of temperatures reveals two relaxation processes, α and β relaxations[1-7].

The commonly accepted explanation for the β relaxation is that it is related to the molecular details of the glass former. However, the mode coupling theory (MCT)[9] suggests that it may be a general dynamical feature of dense disordered systems rather than being specific to the glass under investigation. Moreover, the MCT theoretically demonstrates the existence of the two distinct relaxation processes. The slower process (α) is associated with the diffusive motion and the faster one (β) is attributed to strongly anharmonic motions of a limited number of molecules trapped in cages formed by their neighbors.

On the other hand, computer simulations suggest that the β relaxation represents cooperative localized motions of a small number of molecules within a cage formed by neighboring molecules[10]. On the time scale of the β relaxation , these cages appear frozen. For longer times collective rearrangements continue allowing the eventual relaxation of the cages, which represents the α relaxation.

If one neglects the interaction between different cages then one may model the β relaxation as the superposition of a heterogeneous distribution of independent relaxing regions, the cages. There are several models in the literature which deal with such a situation[11-14]. In all cases, it is assumed that each cluster relaxes exponentially with a size dependent relaxation time. The main simplification of these models is thus the assumption of an exponential relaxation of the independent regions. The slow relaxation dynamics appears when one superposes the contribution of each region over the distribution of cluster sizes. However, the cooperative nature of the dynamics inside each cluster leads, by itself, to a slow relaxation dynamics. In fact, there are several models which do not contain disorder and obtain the slow relaxation as a consequence of the cooperative nature of the dynamics[9,15,16].

In the present work we present a fractal model to describe the main features of the β relaxation in supercooled liquids. We assume that the macroscopic dynamics is given by the superposition of the relaxation of independent mesoscopic regions (cages). Nevertheless, different from previous works, we do not assume that each mesoscopic region relaxes exponentially. In this way we obtain some scaling relations for the average response, in the time and frequency domain. For a particular choice of the scaling exponents we obtain the scaling relations predicted by the MCT. The comparison with recent light scattering data reveals that the scaling exponents of the distribution of cage sizes are universal but the single cage relaxation depends on the detailed material structure.

The paper is organized as follows. In section II we introduce the fractal model for the β relaxation in supercooled liquids and derive some of its predictions. The scaling relations for the normalized relaxation function and the imaginary part of the susceptibility are obtained. Then, in section III we discuss the main results of the model, and

compare them with other theoretical approaches and recent light-scattering data reported in the literature. Finally, the conclusions are given in section IV.

II. FRACTAL MODEL

Computer simulations suggest that the β relaxation represents cooperative localized motions of a small number of molecules within a cage formed by neighboring molecules[10]. On the time scale of the β relaxation, these cages appear frozen. For longer times collective rearrangements continue allowing the eventual relaxation of the cages, which represents the α relaxation. In the following we restrict our analysis to the mesoscopic time scale between the microscopic characteristic time τ_0 and the mean live time of the cages, i.e. we focus our attention in the β relaxation regime.

A. Single cage relaxation

Let s be the number of molecules in a cage and τ_s the characteristic time associated with the cooperative rearrangements of the molecules in a cage of size s. The relaxation in large cages, involving many molecules, is relatively infrequent and is associated with a long time relaxation process. On the contrary, the relaxation in small cages, involving a few molecules, occurs more often and is associated with a short time relaxation process. We thus assume that the characteristic time scales with the cage size according to

$$\tau_s = \tau_0 s^\zeta, \tag{1}$$

where $\zeta > 0$ is a scaling exponent. In the following we measure time in units of τ_0.

τ_s is the only relevant time scale in the β relaxation regime. Hence, the normalized response function will satisfy the scaling law

$$\Phi(s, t) = t^\eta f_1(s^{-\zeta} t). \tag{2}$$

where $f_1(x)$ is a scaling function. On the other hand, $\Phi(s, t)$ has to satisfy the normalization condition

$$\int_0^\infty dt \Phi(s, t) = 1. \tag{3}$$

This constraint carry as a consequence that

$$\eta = -1 \qquad \int_0^\infty dx \frac{f_1(x)}{x} = 1. \tag{4}$$

B. Average relaxation

The cage size follows certain distribution $P(s)$. Computer simulations suggest that the number of molecules involved in cooperative rearrangements is widely distributed[17,18]. Let $s_c \sim \epsilon^{-1/\sigma}$ be a characteristic cage size below with the distribution is scale invariant. We can therefore assume that $P(s)$ satisfies the scaling law

$$P(s) = s^{-\tau} f_2(\epsilon^{1/\sigma} s), \tag{5}$$

where $1 < \tau < 2$ and $\sigma > 0$ are scaling exponents, and $f_2(x)$ is a scaling function with the asymptotic behaviors: $f_2(x \ll 1) \approx$ const. and $f_2(x \gg 1) \ll 1$. ϵ is a control parameter, which characterizes how close is the system from the scale invariant case: $P(s) \sim s^{-\tau}$. It can be related to the mean cluster size through the equation

$$\langle s \rangle \sim \epsilon^{-(2-\tau)/\sigma}. \tag{6}$$

Hence $\langle s \rangle \to \infty$ is equivalent to $\epsilon \to 0$. In supercooled liquids and amorphous solids there is no long range order and, therefore, we expect that the mean cluster size is always finite, i.e. $\epsilon > 0$. We are thus considering the relaxation of scale invariant mesoscopic clusters.

The average normalized response function is given by

$$\Phi(t) = \int_0^\infty ds P(s)\Phi(s,t). \tag{7}$$

Using eqs. (2), (4) and (5) one obtains

$$\Phi(t) = t^{-1-a} f_3(\epsilon^{1/\Delta} t), \tag{8}$$

where

$$a = (\tau - 1)\zeta^{-1}, \qquad \Delta = \sigma/\zeta, \tag{9}$$

$$f_3(x) = \zeta^{-1} \int_0^\infty dy\, y^{a-1} f_1(y) f_2[(x/y)^{1/\zeta}]. \tag{10}$$

$f_3(x)$ is another scaling function, expressed as a function of the previously introduced scaling functions $f_1(x)$ and $f_2(x)$. If $f_2(x)$ is analytical in $x = 0$ then, expanding this function around $x = 0$, from eq. (10) one obtains

$$f_3(x) \approx A - Bx^{1/\zeta}, \tag{11}$$

where

$$A = \zeta^{-1} f_2(0) \int_0^\infty dx\, x^a \frac{f_1(x)}{x} \tag{12}$$

$$B = \zeta^{-1} |\dot{f}_2(0)| \int_0^\infty dx\, x^{a-1/\zeta} \frac{f_1(x)}{x}. \tag{13}$$

Here we assume that the function $f_1(x)$ is such that the integrals in eqs. (4), (12) and (13) converge. Substituting this asymptotic expansion in eq. (8) it results that

$$\Phi(t) \sim \epsilon^{(1+a)/\Delta} [(\epsilon^{1/\Delta} t)^{-1-a} + C(\epsilon^{1/\Delta} t)^{-1+b}], \tag{14}$$

where

$$b = \zeta^{-1} - a, \tag{15}$$

and $C = B/A$. Eq. (14) gives the asymptotic behavior of the response function in the scale invariant region $t \ll \epsilon^{-1/\Delta}$.

C. Susceptibility

The imaginary part of the normalized susceptibility χ'' is related to the normalized response function through the equation

$$\chi''(\omega) = \mathrm{FT}''[\Phi(t)](\omega) , \tag{16}$$

where FT'' denotes the imaginary part of the Fourier transform. Substituting $\Phi(t)$ by its scaling law in eq. (8) one obtains

$$\chi''(\omega) = \omega^a f_4(\epsilon^{-1/\Delta} \omega), \tag{17}$$

where $f_4(x)$ is another scaling function, given by

$$f_4(x) = \int_0^\infty dy \cos(y) y^{-a-1} f_3(y/x). \tag{18}$$

Moreover, in the frequency range $\epsilon^{1/\Delta} \ll \omega \ll 1$ from eqs. (14) and (16) it follows that

$$\chi''(\omega) = \chi''_{\min}\left[a\left(\frac{\omega}{\omega_{\min}}\right)^a + b\left(\frac{\omega}{\omega_{\min}}\right)^{-b}\right], \tag{19}$$

where

$$\chi''_{\min} \sim \epsilon^{a/\Delta} \qquad \omega_{\min} \sim \epsilon^{1/\Delta}. \tag{20}$$

From eq. (19) one concludes that the susceptibility has a minimum $\chi''_{\min}$ at the frequency $\omega_{\min}$.

III. DISCUSSION

In the previous section we have obtained the scaling laws for the normalized relaxation function and the imaginary part of the susceptibility. Now, we proceed to discuss these results and to compare them with other theoretical approaches and experimental data.

The scaling laws in eqs. (2) and (17) are very similar to those obtained by the MCT[9]. In fact, if we take

$$\Delta = 2a, \tag{21}$$

then we obtain the scaling laws of the MCT. This equation constitutes a scaling relation for the scaling exponents a and Δ, which has to be imposed to obtain the results of the MCT. Our formulation thus result more general, while the MCT prediction is contained as a particular case.

From eqs. (9 and 15) one can obtain the exponents τ and ζ, introduced in our fractal model, as a function of a and b, which are usually measured in light scattering experiments in the β regime. It results that

$$\zeta = \frac{1}{a+b}, \qquad \tau = \frac{2a+b}{a+b}. \tag{22}$$

Moreover, if one assumes that (22) is valid then form eq. (9) we obtain

$$\sigma = \frac{2a}{a+b}. \tag{23}$$

We emphasize again that eq. (22), and therefore eq. (23), is valid if one assumes the MCT prediction. Then using some light scattering reports for different supercooled liquids we have calculated these scaling exponents. The results are shown in I and II.

First, we notice that the exponent τ is larger than the one obtained in standard percolation (SP) in three dimensions, $\tau_{SP} = 1.15$. One of the shortcomings of standard percolation theory is that it neglects frustration, which introduces cancellations and hence the possibility of weak correlation, even if the interactions are much smaller than the thermal energy. Thus, standard percolation models are too simple to explain the behavior of glass forming liquids. This conclusion has been also pointed out for spin glasses[20]. The inclusion of frustrated effects in percolation models is relatively recent[21]. The frustrated percolation (FP) model suggests that in glass-forming liquids there is a percolation temperature T_{FP} above T_g, where frustration effects starts to be manifested. This transition leads to highly correlated localized clusters.

Thus, we can describe the cage formation in supercooled liquids using a frustrated percolation model. Unfortunately, simulations in three dimensions are not yet available. In any case, it is expected that the exponents τ and σ are larger in FP than in SP. Frustration effects inhibit the formation of long range structures and, therefore, the distribution of cluster sizes in FP should decay faster than in SP, i.e. $\tau_{SP} < \tau_{FP}$. Moreover, the temperature T_c may be identified with T_{FP} and $\epsilon = |T - T_{FP}|$.

The data displayed in tables I and II has been divided in different groups attending to the structure of the glass formers. In the first class we have the two simple molecular glass formers ortophenyl and salol. These materials have a very simple structure with symmetric (Van der Waals like) interactions among their molecules. They are fragile glass formers and the scaling exponents a and b in both materials are quite similar. Molecular glass formers thus show similar static and dynamic behavior. Frustration may arise when local arrangements of molecules kinetically prevent all the molecules from reaching ordered close-packed configurations. Frustration effects have in this case a kinetic origin. In the second group we find the glass formers glycerol and B_2O_3. Glycerol is a fragile glass former which has a hydrogen-bonded network structure. B_2O_3 is a strong glass former and has a covalent bonded network structure. Hence, these materials are different in relation with the temperature dependence of the static viscosity. However, the scaling exponents a and b, which characterize the dynamical properties, are in both materials quite similar. The difference in the temperature dependence of the static viscosity can be associated to the strength of the bonds. The hydrogen bonds are weaker than the covalent ones and, therefore, the network structure in grycerol is more sensitive to temperature shift than in B_2O_3. The common factor in these glass formers is the existence of network structures. We thus expect that frustration is mainly determined by the competition of different interactions generated by the multiple random bond network configurations. The existence of constrained bond angles or lengths leads to some optimized network structure, where some bonds will not satisfy these constrains and become partially broken (frustrated). Frustration effects have, in this case, a structural origin. Finally, in the third and fourth group we found the ionic glass former CKN and polymers, respectively. The exponents a and b are in both groups very different and greater than those reported for the first two groups. The origin of the frustration effects in these materials is less clear since we do not understand their structure well enough.

However, in spite that a and b change from one group to another, the scaling exponents of the distribution of cages sizes τ and σ are very similar. We found $\tau \approx 1.34$ and $\sigma \approx 1.69$ (an exception are the polymers PPG and PET which are discussed below). Thus we have found a universal behavior for the distribution of cages sizes. On the contrary, the scaling exponent ζ results material dependent. This scaling exponent is related to the single cage relaxation and, therefore, one may conclude that the single cage relaxation depends on the detailed structure of the glass former. The universal behavior can only appear when the single cage relaxation is averaged over the distribution of cages sizes.

In the case of the polymers PPG and PET the exponent σ deviates from that observed in the others glass formers. However, the scaling exponent τ is similar to the one observed in the other glass formers. This deviation may be associated with the fact that the relation between τ and the light scattering exponents a and b were obtained using general considerations, while that for σ were obtained assuming that the MCT is correct. Hence, one may conclude that the MCT cannot be applied to polymers. Off course, to validate this conclusion a more extensive experimental analysis is needed.

IV. SUMMARY AND CONCLUSIONS

We have presented a fractal approach to the β relaxation in supercooled liquids. The main ingredients of the model are the existence of scaling laws for the single cage normalized relaxation function and for the distribution of cage sizes. In this way we have obtained the scaling laws for the average response, which for a particular choice of scaling exponents lead to those obtained by the MCT.

We have obtained some scaling relations between the scaling exponents introduced in the model and those obtained from the fit to light-scattering data. Using these scaling relations and the reports for some light-scattering experiments we have found the β relaxation is indeed a general dynamical feature of dense disordered systems, which does not depend on the specific glass former under investigation.

The scaling exponents distribution of cage sizes appears to be universal. The material dependence of the exponents a and b obtained from light scattering data is a consequence of the non-universality of the single cage relaxation, which depends on the detailed structure of the glass former. Moreover, the scaling exponent τ and σ were found larger than the one obtained in standard percolation in three dimensions. This discrepancy was attributed to frustration effects, and the cage formation was associated to a frustrated percolation problem.

Our approach reveals that the MCT scaling relations may not be valid for polymers, but a more extensive analysis of experimental data is needed. The present work may be used as a guide for further experimental investigations of the β relaxation in supercooled liquids and glasses, in order to check our results.

ACKNOWLEDGEMENTS

[1] *Dynamics of glass transition and related topics*, Proceedings of the 7th Yukawa International Seminar, Ed. by T. Odagaki, Y. Hiwatari, and J. Matsui, Prog. Theor. Phys. Suppl. **126** (1997).

[2] G. Li, W. M. Du, A. Sakai, and H. Z. Cummins, Phys. Rev. A **46**, 3343 (1992).

[3] H. Z. Cummins, G. Li, W. Du, Y. H. Hwang, and G. Q. Shen, ref.[1] page 21.

[4] D. Sidebottom, R. Bergman, L. Börjesson, and L. M. Torell, Phys. Rev. Lett. **71**, 2260 (1993).

[5] J. Wuttke, J. Hernandez, G. Li, G. Goddens, H. Z. Cummins, F. Fujara, W. Petry, and H. Sillescu, Phys. Rev. Lett. **72**, 3052 (1994).

[6] G. Li, W. M. Du, X. K. Chen, and H. Z. Cummins, Phys. Rev. A **45**, 3867 (1992).

[7] D. L. Sidebottom, R. Bergan, L. B́orjesson, and L. M. Torell, Phys. Rev. Lett. **68**, 3587 (1992).

[8] H. Eliasson, B.-E. Mellander and L. Sjögren, J. Non Cryst. Solids (to appear).

[9] W. Götze, in *Liquids, Freezing and the Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (North-Holland, Amsterdam, 1991); W. Götze and L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992).

[10] G. Wahnström, Phys. Rev. A **44**, 3752 (1991).

[11] C. Domb, A. A. Maradudin, E. W. Montroll, and G. H. Weiss, Phys. Rev. **115**, 24 (1959).

[12] M. H. Cohen and G. Grest, Phys. Rev. B **24**, 4991 (1981).

[13] A. Vázquez and O. Sotolongo-Costa, J. Chem. Phys. **106**, 3772 (1997); A. Vázquez, O. Sotolongo-Costa, and F. Brouers, J. Phys. Soc. Jpn. **66**, 2324 (1997).

[14] R. W. Chamberlin, J. Appl. Phys. **76**, 6401 (1994).

[15] K. L. Ngai, Comments Sol. Stat. Phys. **9**, 127 (1980).

[16] S. Franz and J. Hertz, Phys. Rev. Lett. **74**, 2114 (1995).

[17] I. Ohmine, H. Tanaka, and P. G. Wolynes, J. Chem. Phys. **89**, 5852 (1988).

[18] H. Miyagawa, Y. Hiwatari, B. bernu, and J. P. Hansen, J. Chem. Phys. **88**, 3879 (1988).

[19] D. Stauffer, Phys. Rep. **54**, 1 (1979).

[20] K. Binder and K. Schröder, Phys. Rev. B **14**, 2142 (1976).

[21] A. Coniglio, F. di Liberto, G. Monroy, and F. Peruggi, Phys. Rev. B **44**, 1265 (1991); S. Scarpetta, A. de Candia, and A. Coniglio, Phys. Rev. E **55**, 4943 (1997); A. Coniglio, Prog. Theor. Phys. Suppl. **126**, 281 (1997).

Glass former	a	b	ζ	τ	Ref.
salol	0.33	0.64	1.0	1.3	[2]
orthophenyl	0.33	0.65	1.0	1.3	[3]
B_2O_3	0.31	0.62	1.1	1.3	[4]
glycerol	0.32	0.61	1.1	1.3	[5]
$Ca_{0.4}K_{0.6}(NO_3)_{1.4}$ (CKN)	0.27	0.46	1.4	1.4	[6]
poly(propylene glycol) (PPG)	0.23	0.36	1.7	1.4	[7]
poly(ethylene terephthalate) (PET)	0.27	0.44	1.4	1.4	[8]

TABLE I. The scaling exponents ζ and τ for different supercooled liquids, obtained using the values of a and b reported in the corresponding references.

Glass former	Δ	σ
salol	0.66	0.68
orthophenyl	0.66	0.67
B_2O_3	0.62	0.69
glycerol	0.64	0.69
$Ca_{0.4}K_{0.6}(NO_3)_{1.4}$ (CKN)	0.54	0.70
poly(propylene glycol) (PPG)	0.46	0.77
poly(ethylene terephthalate) (PET)	0.54	0.76

TABLE II. The scaling exponents Δ and σ for different supercooled liquids. These exponents were obtained assuming that the MCT predictions are valid.